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Hierarchical Self-Assembly of Toroidal Micelles into Multi-Dimensional Nanoporous Superstructures

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ABSTRACT: Materials with controlled porosity play a predominant role in industrial and domestic applications. Although a rich array of methods has been developed to tune the pore size in a broad range (from <1 nm to >1 μ m), the fabrication of functional materials with a fully open porous structure with pore size of sub-100 nm has remained a significant challenge. Here, we report the hierarchical assembly of block copolymer toroidal micelles with an intrinsic hole into multi-dimensional nanoporous superstructures (pore size 85–90 nm) by modulation of interparticle interactions. The toroids aggregate into oligo-supermicelles or 2D hexagonal arrays through van der Waals interactions upon drying on a substrate, while synergistic hydrogen bonding interactions further promote the formation of 3D nanoporous superstructures directly in solution. Thus, toroidal micelles can be manipulated as a type of distinctive building block to construct nanoporous materials.

Porous materials are of critical importance in catalysis, separations, and many other applications.¹ Over the past few decades a variety of different approaches, such as electrochemical etching of aluminum oxide,² breath figure fabrication,³ templating of mesoporous silica,⁴ metal-organic and covalent organic framework (MOFs and COFs, respectively) formation,⁵ and the creation of organic cage solids,⁶ have been developed to prepare ordered porous materials. The MOF/COF and cage strategies primarily utilize molecular building blocks to construct pores either through the formation of extended polymeric structures or via supramolecular assembly of discrete species possessing an intrinsic cavity. Indeed, directed self-assembly is emerging as a versatile approach to fabricate porous media with building blocks that span across several length scales and include molecules,⁷ DNA,⁸ polymers,⁹ and colloidal nanoparticles.¹⁰ Nevertheless, the uniformity of pores arising from the cavities generated during packing and the precise control of pore size generally remain lingering technological challenges.

Self-assembled nanoscopic toroids have recently attracted considerable attention due to their unique geometry and potential utility in materials fabrication.^{11,12} Using a rich array of species, including small molecules¹¹ and block copolymers (BCPs),¹² the ring diameter (*ca.* 10 – 200 nm) and chemistry can be adjusted over a significant range. These features suggest that toroidal micelles are promising building blocks for the fabrication of complex functional assemblies, although advances in this direction remain rather limited.^{12d,13,14} Moreover, their inherently hollow nature also provides the possibility to generate pores. Herein, we report the formation of multi-dimensional nanoporous superstructures through hierarchical self-assembly of BCP toroids by modulation of interparticle interactions.

Toroidal micelles were prepared by solution self-assembly of a PI₁₀₄₀-*b*-P2VP₂₀₀ diblock copolymer (PI = polyisoprene, P2VP = poly(2-vinylpyridine), and the subscripts denote the degree of polymerization, Fig. S1) in a mixture of tetrahydrofuran (THF) and ethanol (1:4 v/v) according to a procedure described by Chang and

coworkers.^{12d} Transmission electron microscopy (TEM) analysis of drop-cast samples indicated that the toroidal micelles with a PI core and a P2VP corona possessed a low dispersity ring-like morphology (Fig. S2) and a number-average diameter (D_n) of 113 nm ($D_w/D_n = 1.03$, where D_w denotes the weight-average diameter).

Initially, we explored the hierarchical self-assembly of the toroidal micelles through the utilization of van der Waals interactions. Convective self-assembly, which involves the evaporation of solution dispersions, has been established as a promising route to fabricate close-packed colloidal superstructures from a diverse range of nanoparticles.¹⁵ However, attempts involving solvent evaporation from a relatively concentrated solution of the toroidal micelles were unsuccessful at inducing significant aggregation (Fig. S3a), presumably due to insufficient interparticle interactions under these conditions.¹⁶ In striking contrast, we found that the toroids aggregate into 2D superstructures upon drying from a solution with added PFS-*b*-P2VP (PFS = polyferrocenyldimethylsilane)¹⁷ in the form of unimers in THF (Fig. 1).

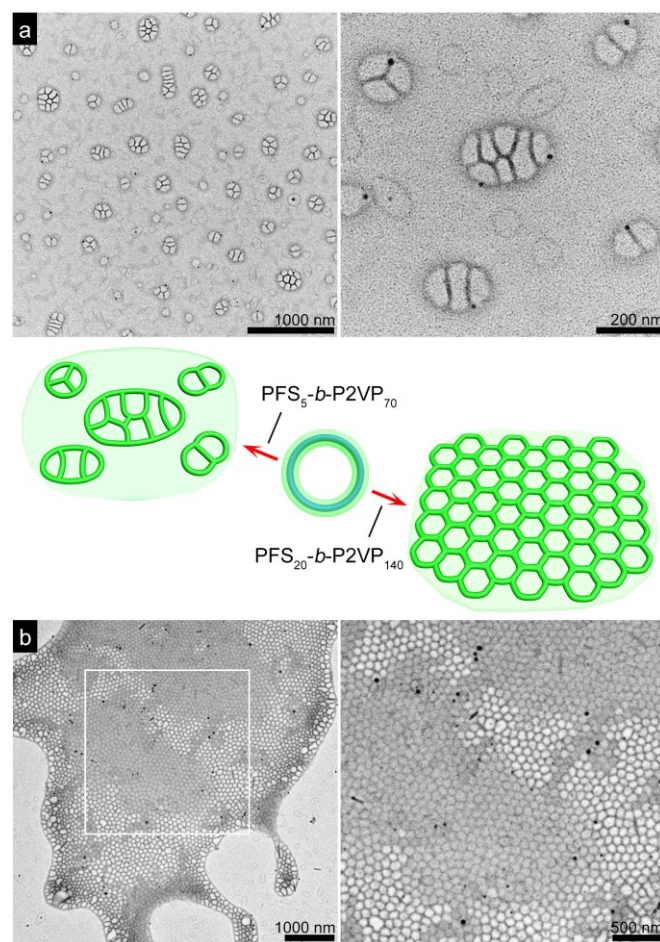


Figure 1. TEM images and schematic illustrations of (a) oligomeric supermicelles and (b) hexagonal arrays formed by 2D association of toroidal micelles in 1:4 (v/v) THF/ethanol

in the presence of PFS₅-*b*-P2VP₇₀ (PI₁₀₄₀-*b*-P2VP₂₀₀ : PFS₅-*b*-P2VP₇₀ = 2:1, mass ratio) and PFS₂₀-*b*-P2VP₁₄₀ (PI₁₀₄₀-*b*-P2VP₂₀₀ : PFS₂₀-*b*-P2VP₁₄₀ = 4:1, mass ratio), respectively.

The morphology of the resulting 2D superstructures varied with the specific PFS-*b*-P2VP block copolymer added. In the presence of PFS₅-*b*-P2VP₇₀ unimers, the toroidal micelles preferred to associate to form oligomeric supermicelles (Fig. 1a) with aggregation numbers ranging from 2 to >10 (Figs. S4a,b). “Trimers” displayed only two morphological variants (Figs. 1a, S4c), while “tetramers” exhibit three isomers (Fig. S4d). As expected, the situation became far more diverse for the higher-aggregation-number species (Fig. S4a). On the other hand, when PFS₂₀-*b*-P2VP₁₄₀ was added, association occurred over a much larger region (> 100 μm²) and yielded planar arrays (Figs. 1b, S5). The toroidal micelles were predominantly arranged on a 2D hexagonal lattice with a mean pore-to-pore distance of *ca.* 90 nm. This value is smaller than the diameter of the toroidal building blocks, indicating significant shrinkage during packing.

Control experiments indicated that the presence of the PFS block is essential for the 2D hierarchical self-assembly to occur as the addition of P2VP homopolymers failed to induce any obvious association of the toroidal micelles after solvent evaporation (Figs. S3b,c). As PFS is also hydrophobic, it would be expected to rapidly precipitate in an amorphous form on the toroidal PI core under the polar solvency conditions used. This process appears to increase the inter-toroidal interactions sufficiently to drive the 2D assembly process. Consistent with this explanation, increased electron density contrast is evident from the cores in the TEM images (see Fig. 1a right, Fig. S4c). Moreover, the extent of toroidal aggregation was higher for the case of the block copolymer with a longer PFS block (PFS₂₀ versus PFS₅).

In a second set of experiments we attempted to induce direct association of toroidal micelles in solution through the utilization of stronger, non-covalent interactions. Previous work has shown that hydrogen (H)-bonding between nitrogen-based H-bond acceptor and H-bond donor hydroxyl groups can be used to construct various hybrid nanomaterials and complex hierarchical nanostructures from block copolymer micelles.¹⁸ We therefore explored whether toroidal micelles with a P2VP corona could be linked together by a homopolymer “glue” bearing hydroxyl groups. To evaluate this idea, we tethered hydroxyl groups to polymethylvinylsiloxane (PMVS) homopolymer via thiol-ene click chemistry.^{18e} However, upon addition of the resulting homopolymer (PMVSOH₂₈₅) to a solution of the toroidal PI₁₀₄₀-*b*-P2VP₂₀₀ micelles (in either methanol, ethanol or 1:4 v/v THF/ethanol) (PI₁₀₄₀-*b*-P2VP₂₀₀ : PMVSOH₂₈₅ = 2:5, mass ratio) no obvious hierarchical association was detected; only discrete toroids remained upon solvent evaporation according to TEM (Fig. S6).

On the basis of the aforementioned successful formation of oligomeric supermicelles, we therefore explored whether the H-bonding capability of a hydroxyl-functionalized PMVS would be effective at inducing stacking interactions when combined with a PFS segment (Fig. 2a). A series of PFS-containing BCPs with a hydroxyl-functionalized PMVS block was therefore prepared (Fig. S1) and, upon the addition of PFS₄₈-*b*-[PMVS(OH)₂]₃₂₆ unimers (PI₁₀₄₀-*b*-P2VP₂₀₀ : PFS₄₈-*b*-[PMVS(OH)₂]₃₂₆ = 1:1, mass ratio), the toroidal micelles rapidly aggregated and formed visible agglomerates suspended in solution (Fig. S7, inset) and subsequent TEM analysis indicated that the particles consisted of close-packed toroidal micelles (Figs. 2b,c, S7, S8). Along the periphery, the toroid micelles were again arranged in 2D fashion with a pore-to-pore distance of *ca.* 85 nm. In contrast, the thicker central areas displayed a sponge-like superstructure wherein the toroidal micelles were packed in a more complex 3D array (Figs. S7, S8). To unveil the stacking mechanism, energy dispersive X-ray spectroscopy mapping (Fig. S9) and Fourier transform infrared spectroscopy (Fig. S10) were conducted. The results clearly verified the uniform association of the toroidal micelles with PFS BCPs and the existence of H-bonding interactions, respectively. The porous feature of the sponge-like superstructure was demonstrated by atomic force microscopy (AFM) (Figs. 2d,e, S11, S12). With toroidal micelles observed to be closely packed across a relatively large area measuring over 100 μm^2 on the top surface (Fig. S11), porous structures in deeper region were also visible through defects in the upper layer (Figs. 2d).

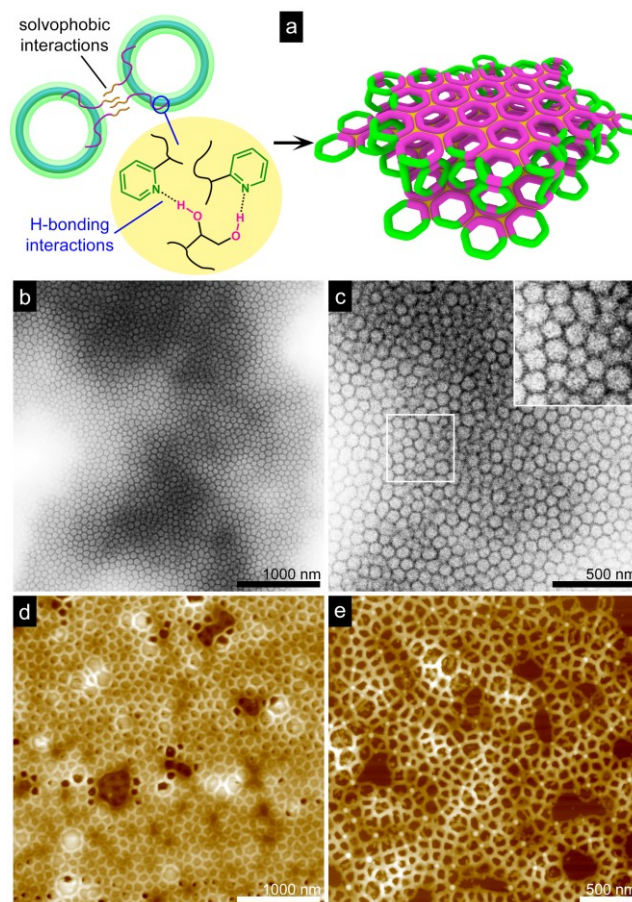


Figure 2. (a) Formation of sponge-like nanoporous superstructures through 3D association of toroidal micelles in 1:4 (v/v) THF/ethanol induced by the addition of PFS₄₈-*b*-[PMVS(OH)₂]₃₂₆ unimers (PI₁₀₄₀-*b*-P2VP₂₀₀ : PFS₄₈-*b*-[PMVS(OH)₂]₃₂₆ = 1:1, mass ratio) and, corresponding (b and c) TEM and (d and e) AFM images. The samples in (d and e) were prepared on a silicon wafer and a highly oriented pyrolytic graphite (HOPG) substrate, respectively.

Transmission electron microtomography (TEMt) analysis further revealed that the sponge-like superstructure possessed a continuous nanoporous framework with fairly regular pores passing through the entire aggregate (Fig. 3, Movie S1) in similar fashion to an open-cell foam. The thicker region identified by the square primarily consisted of two layers of planar frameworks (Fig. 3, bottom right, indicated by yellow and pink colours, respectively), which were isolated and connected by a series of interplanar toroidal micelles (Movie S1).

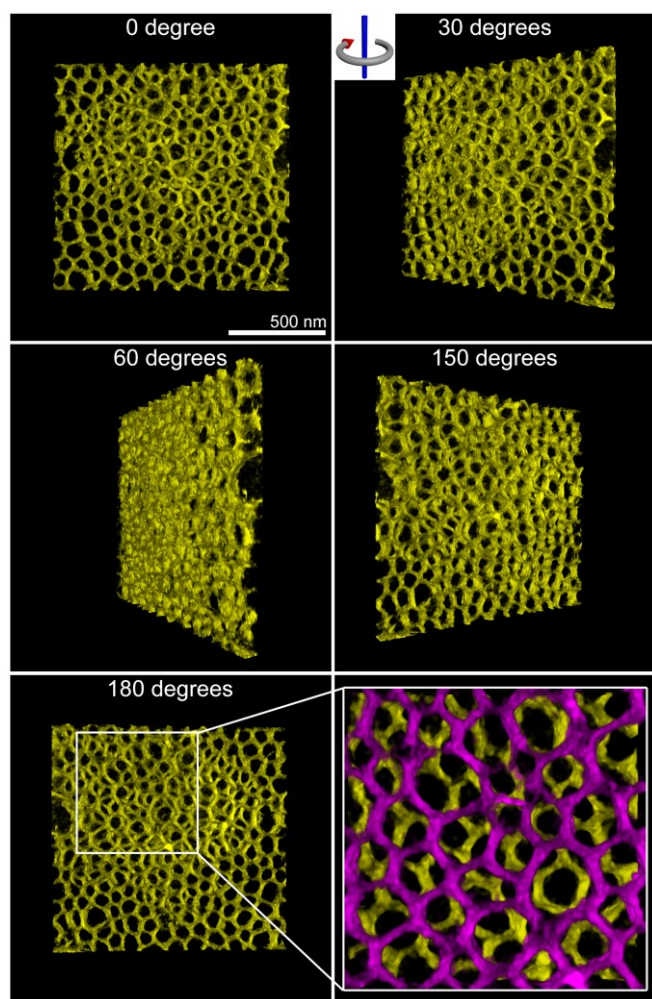


Figure 3. 3D TEMT images of a nanoporous superstructure displayed at various tilt angles (labelled).

Furthermore, in order to validate the toroidal association in solution, the toroidal micelles were labelled with a green fluorescent dye prior to hierarchical self-assembly (Fig. 4a), and the solution was subsequently studied by confocal laser scanning microscopy (CLSM) and stimulated emission depletion (STED) microscopy. It was apparent that the superstructures exist in solution (Figs. 4b,c, S13). The toroidal micelles were clearly close-packed, although the internal structure was indiscernible due to the resolution limit of STED microscopy (Figs. 4d,c). Nonetheless, these observations provided tangible evidence that the toroidal micelles undergo association in solution, instead of occurring as a drying effect that arises during solvent evaporation.

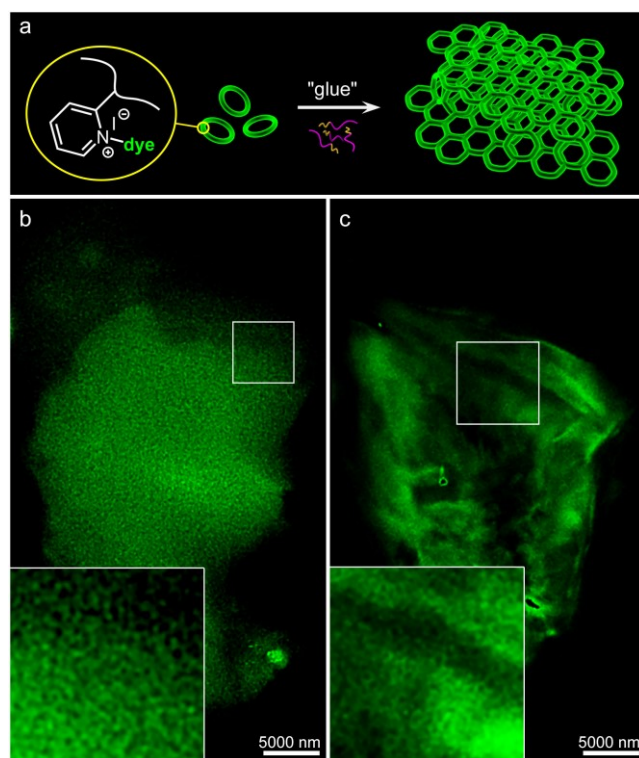


Figure 4. (a) Schematic illustration of the formation of green fluorescent dye-labeled 3D nanoporous superstructures in solution and (b and c) corresponding STED images.

The formation of a 3D nanoporous superstructure depends significantly on the nature of the polymeric "glue" employed (Fig. S14). Thus, both $\text{PFS}_{48}\text{-}b\text{-}[\text{PMVS}(\text{OH})_2]_{326}$ and $\text{PFS}_{20}\text{-}b\text{-}[\text{PMVS}(\text{OH})_2]_{120}$, each with two hydroxyl groups per repeat unit (Fig. S1), triggered the aggregation of toroidal micelles into nanoporous superstructures in ethanolic media (Figs. S14b,e). In marked contrast, $\text{PFS}_{20}\text{-}b\text{-}[\text{PMVS}(\text{OH})_2]_{120}$ and $\text{PFS}_{20}\text{-}b\text{-}[\text{PMVS}(\text{OH})_2]_{560}$, with only one hydroxyl group tethered to each repeat unit, were unable to promote large-scale association, although small oligomeric supermicelle aggregates were observed (Figs. S14h,k). The nature of the solvent also demonstrated an important effect on the formation of nanoporous superstructures (Fig. S14). In the presence of $\text{PFS}\text{-}b\text{-}[\text{PMVS}(\text{OH})_2]_n$, for example, the association of toroidal micelles in ethanol was very similar to that observed in 1:4 (v/v) THF/ethanol (Figs. S14b,c,e,f). However, in methanol, an even poorer solvent than ethanol for PFS, $\text{PFS}_{48}\text{-}b\text{-}[\text{PMVS}(\text{OH})_2]_{326}$, with a relatively long PFS block, self-organized into small spherical micelles (core diameter < 10 nm) that surrounded the toroidal micelles but failed to induce obvious intermicellar association (Fig. S14a). Interestingly, $\text{PFS}_{20}\text{-}b\text{-}[\text{PMVS}(\text{OH})_2]_{120}$ preferred to condense at different positions along the rims of toroidal micelles to form a variety of patchy assemblies (Fig. S14d).

The influence of both the structure of the added polymer and the dispersing solvent on nanoporous superstructure formation suggests that significant H-bonding interactions are required for the well-defined 3D hierar-

chical association of toroidal micelles. Although more comprehensive studies are needed (and are underway), the higher density of hydroxyl groups in PFS-*b*-PMVS(OH)₂ enhances the H-bonding interactions, which appears to promote the formation of nanoporous superstructures. In a very poor solvent for PFS, the added PFS-based BCPs are expected to aggregate first and their association with the toroidal micelles might then be restricted to localized regions.

In summary, we have demonstrated two distinct routes utilizing either van der Waals or H-bonding interactions to promote the lateral hierarchical self-assembly of toroidal micelles into 2D and 3D superstructures, respectively, which is distinct from the previously reported tubular nanostructure formed by face-to-face stacking of toroidal assemblies.¹³ The present work provides a viable strategy for the construction of nanoporous planar films or bulk materials by the association of toroidal nanostructures as building blocks. In principle, the pore size can be regulated by manipulating the toroid diameter, thereby permitting the storage or separation of various guests (such as proteins or viruses). Moreover, the function of such nanoporous materials might be flexibly tuned by precise design of the toroid chemistry so that core- or shell-crosslinking chemistry could be used to “lock-in” the assemblies.^{9a,19} Future work will also focus on an exploration of more complex nanoporous superstructures generated with larger nanomaterials (for example, cylindrical micelles, Fig. S15) as the “glue”.

ASSOCIATED CONTENT

Supporting Information. Experimental details and additional results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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